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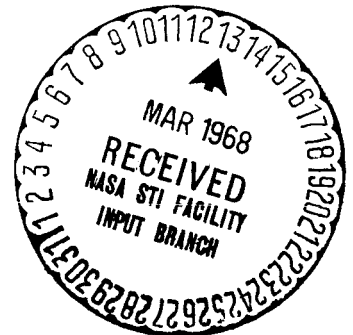
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# CALCULATING THE SURFACE ENERGY OF METALS WITH A BODY-CENTERED LATTICE

Yu. S. Avraamov and A. G. Gvozdev

ABSTRACT. The values are calculated for the surface energies  $\sigma$  and temperature coefficient of surface energy  $d\sigma/dT$  in metals with a body-centered lattice for surfaces (100) (110) allowing for the effect of bonds with the second coordination sphere.

In [1], the value of the surface energy  $\sigma$  in transformer steel for various crystallographic planes was measured using the method of "zero" creep. For the (110) plane in a helium atmosphere,  $\sigma = 1400 \text{ erg/cm}^2$ . However, the absence in the literature of data on the surface energy of transformer steel makes it difficult to critically evaluate experimental results. Because of this, it is of interest to compare the experimental value of surface energy for transformer steel with the theoretical calculations.

Presently, the theory of the surface energy of metals has not as yet made it possible to calculate the value of the surface energy with a satisfactory degree of accuracy. Therefore, in calculations we use empirical and semi-empirical formulas, which relate the surface energy to the metal's physical properties (sublimation heat, electron work function, etc.

The relationship between the surface energy and the sublimation heat may be established by working from the following simple considerations. At  $0^\circ\text{K}$ , the sublimation heat  $(Q_0)$  characterizes the strength of the bonds between the atoms in the metal [2]. If we consider the surface energy of the material as necessary for the transfer of atoms from the crystal body to its surface, i.e. as the energy of the ruptured atomic bonds located on the surface, we may write

$$\sigma_0 = \frac{1}{2} n \Delta k \frac{Q_0}{k}, \quad (1)$$

where  $k$  is the coordination number of atoms within the metal,  $\Delta k$  is the number of ruptured bonds in the atom on the surface;  $n$  is the number of atoms per unit surface;  $\sigma_0$  is the value of the surface energy ( $0^\circ\text{K}$ ). The value  $Q_0/k$  characterizes the energy for a single atomic bond. The number of atoms per unit surface equals  $n = k_s/S$ , where  $k_s$  is the number of atoms entering the elementary plane cell;  $S$  is the number of cells.

The volume of the elementary cell may be expressed in the following manner:

$$V = \frac{k_v A}{\rho N}, \quad (2)$$

where  $k_v$  is the number of atoms entering the volumetric elementary cell,  $A$  is the atomic weight;  $\rho$  is density and  $N$  is the Avogadro number. On the other hand,

for a simple cubic lattice  $V = a^3$  and  $S = a^2$  where  $a$  is the lattice period.

Using expression (2), for value  $S_0$  per single mole we obtain

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$$S_0 = NS = f_{hkl} N^{1/2} \left( \frac{Ak_V}{\rho} \right)^{1/2}, \quad (3)$$

where  $f_{hkl}$  is the packing factor characterizing the density of atoms in the plane under consideration. Then the number of atoms per unit of surface.

$$n = \frac{k_S}{f_{hkl} N^{1/2} \left( \frac{Ak_V}{\rho} \right)^{1/2}}. \quad (4)$$

Substituting the value  $n$  from equation (4) into equation (1), we obtain

$$\sigma_0 = \frac{1}{2} \frac{k_S \Delta k Q_0}{f_{hkl} N^{1/2} \left( \frac{Ak_V}{\rho} \right)^{1/2} k}. \quad (5)$$

Expression (5) permits us to calculate the value of the surface energy of the metal for various crystallographic planes at  $0^\circ\text{K}$ . In order to compare the surface energy calculated according to equation (5) with experimental values, we must know the temperature coefficient for the surface energy  $d\sigma/dT$ . S. N. Zadumkin [2] proposed a formula permitting us to calculate the values for the

$$\frac{d\sigma}{dT} = -3RT \ln 2 \frac{\Delta k}{k} n. \quad (6)$$

Using the given expression, we obtain an equation for calculating the surface energy of the metal at any temperature.

$$\sigma = \frac{1}{2} \frac{k_S \Delta k}{f_{hkl} N^{1/2} \left( \frac{Ak_V}{\rho} \right)^{1/2} k} (Q_0 - 6RT \ln 2). \quad (7)$$

We calculated the value for the surface energy of pure iron for the planes (110) (100) in accordance with equation (5). Because the relationship between the surface energies and the sublimation heat is valid for  $T = 0^\circ\text{K}$ , we must convert the experimental values of the sublimation heat. Rabinowitsch E., and Thilo E. [3] conducted such a conversion for several metals, using the equation

$$Q_0 = Q_T + 3RT, \quad (8)$$

where  $Q_0$  is the sublimation heat for  $0^\circ\text{K}$ ,  $Q_T$  is the sublimation heat for  $T^\circ\text{K}$  and  $R$  is the gas constant.

According to the data from [4], for  $\alpha$ -iron  $Q_{al} = 92.5$  kcal/mole and  $Q_m = 3.65$  kcal/mole. Using the values  $Q_{al}$  and  $Q_m$ , from formula (8) we obtain the value  $Q_0 = 4.5 \cdot 10^{12}$  erg/mole for iron.

In calculating the total amount of ruptured bonds, the effect of distant

neighbors was noted. In a metal with a body-centered lattice, each atom forms eight bonds with its nearest neighbors at a distance  $r_1 = a\sqrt{3}/2$  and 6 weaker bonds with atoms of the second coordination sphere located at a distance  $r_2 = a$ . For a body-centered cubic lattice, the ratio  $r_2/r_1 = 1.15$ ; then for a face-centered simple cubic and hexagonal close-packed lattice,  $r_2/r_1 = 1.41$ .

Whence we may expect that the effect of a neighbor from the second coordination sphere will be felt more strongly in metal with body-centered cubic lattices. This must be taken into account in calculating the value of the surface energy. /407

According to [5], the forces of the bonds between atoms decrease inversely proportionally to the distance in the seventh power, i.e.  $1/r^7$ . Taking the energy of the closest atom bond as the distance  $r_1$   $\epsilon_1 = \epsilon$ , we obtain the bond energy for the second coordination sphere  $\epsilon_2 = 0,377 \epsilon$ . The total bond energy for the atom with its closest neighbor within the metal equals  $8\epsilon_1 + 6\epsilon_2 = 10,02\epsilon$ . Then the energy for the single bond is  $\epsilon = Q_0/10,02$ .

Allowing for the effect of a neighbor from the second coordination sphere we calculated the surface energy (See Table 1) according to equation (5) for  $\alpha$ -iron for the planes (110) (100). Substituting the values  $A = 55.85$ ,  $N = 6.023 \cdot 10^{23}$  atom/mole and  $\rho = 7.87$  G/cm<sup>2</sup> into equation (5), for the plane (110) at 0°K we obtain  $\sigma_{\alpha\text{-Fe}} = 1770$  erg/cm<sup>2</sup> and for the (100) plane we obtain  $\sigma_{\alpha\text{-Fe}} = 1980$  erg/cm<sup>2</sup>.

The ratio between the surface energies  $\sigma$  for these planes  $\sigma_{(110)}/\sigma_{(100)} = 1:1.12$ , i.e. the  $\sigma$  for the (100) plane is approximately 10% greater than  $\sigma$ , for the (110) plane. If, however, in calculating for metals having a body-centered cubic lattice we do not take into account the effect of the atoms from the second coordination sphere, the ratio  $\sigma_{(110)}/\sigma_{(100)} = 30\%$ . Such a difference in the value of the surface energies was calculated by Skapski [6], who did not take into account the effect of distant neighbors and therefore obtained inaccurate values for the  $\sigma$  of  $\alpha$ -iron; for the (110) plane he obtained  $\sigma = 1104$  erg/cm<sup>2</sup> and for the (100) plane he obtained  $\sigma = 1602$  erg/cm<sup>2</sup>.

TABLE 1. CALCULATING THE SURFACE ENERGY OF  $\alpha$ -IRON ACCORDING TO FORMULA (5) \*

Crystallographic Plane	$k_s$	$k_v$	$\Delta k_1$	$\Delta k_2$	$\Delta k_3$	$k$	$\frac{\Delta k}{k}$	$\frac{\Delta k}{k} \cdot S$	$\sigma$ , erg/cm <sup>2</sup>
(110)	2	2	2	2	2,754	10,02	0,275	$7,4 \cdot 10^8$	1770
(100)	1	2	4	1	4,377	10,02	0,457	$4,96 \cdot 10^8$	1980

Note. (Ruptured) bonds at the distance  $r_1$  is  $\Delta k_1$  and at the distance  $r_2$   $\Delta k_2$

\*Translator's note -- Commas indicate decimal points.

To compare the value for the surface energy of an  $\alpha$ -iron in plane (110) calculated according to equation (5) with the experimental values for transformer steel from [1], we must note the temperature coefficient of the surface energy  $d\sigma/dT$  for the (110) plane and the surface activity of the silicon in this steel.

The temperature coefficient for the surface energy of the  $\alpha$ -iron in the (110) plane calculated in accordance with formula (6) and with allowance made for the effect of neighbors from the second coordination sphere =  $-0.138$  erg/cm<sup>2</sup> · deg. Then for a temperature of 1380°C, at which the measurements were taken in [1], we obtain the value  $\sigma_{(110)} = 1540$  erg/cm<sup>2</sup>.

Works [7] and [8] studied the effect of silicon on the surface energy of iron and it was found that 1% silicon lowers the value of  $\sigma$  by 10-15 erg/cm<sup>2</sup>. Consequently, the 3% silicon in transformer steel will lower the value of the surface energy by approximately 40 erg/cm<sup>2</sup>. Thus, for Fe - 3% Si alloys, the calculated value of the surface energy for the (110) plane at 1380°C equals approximately 1500 erg/cm<sup>2</sup>. According to [1], the experimental value for the surface energy of transformer steel in the (110) plane equals 1400 erg/cm<sup>2</sup>. If we also take into account that the result for the measurement for  $\sigma$  might be affected by admixtures as well as silicons (the total of admixtures equals 0.2 wt% [1]), the correspondence between experimental value of  $\sigma = 1400$  erg/cm<sup>2</sup> for the (110) plane with the calculated value  $\sigma = 1500$  erg/cm<sup>2</sup> must be recognized as good. /408

Taking into account equations (5) to (7) the surface energy and the temperature coefficient of the surface energy were calculated for planes (110) (100), for metals with a body-centered cubic lattice (Table 2). In doing so, we also took into account the effect of neighbors from the second coordination sphere. The calculated values for the surface energy of metals with a body-centered cubic lattice and the experimental data corresponded well.

TABLE 2. CALCULATED AND EXPERIMENTAL VALUES OF SURFACE ENERGY AND  $d\sigma/dT$  FOR METALS WITH BODY-CENTERED CUBIC LATTICES

Metal	$Q_0 \cdot 10^{-12}$ , erg/mole	A	$\rho$ , g/cm <sup>3</sup>	$\sigma_0$ , erg/cm <sup>2</sup>		$d\sigma/dT$ , erg/cm <sup>2</sup> deg.		Comparison of calculated and experimental values for $\sigma$		
				(100)	(110)	(100)	(110)	T, °K	$\sigma_{calc}$ , erg/cm <sup>2</sup>	$\sigma_{exp}$ , erg/cm <sup>2</sup>
Li	1,58	6,94	0,534	465	414	-0,004	-0,032	459	417	400-430
Na	1,26	23,00	0,97	249	222	-0,070	-0,032	370	223	190-290
K	2,08	39,10	0,86	266	236	-0,015	-0,040	333	250	100-400
Nb	4,65	92,91	8,57	1550	1380	-0,117	-0,105	1403	1330	1100
$\beta$ -Ti	4,53	47,90	4,31	1430	1330	-0,115	-0,103	1933	1270	1325
$\alpha$ -W	8,44	183,92	19,3	3050	2730	-0,128	-0,114	3653	2490	2680
Mo	6,45	95,95	10,2	2350	2100	-0,129	-0,115	2903	1900	2240
V	4,44	50,95	6,1	1760	1565	-0,140	-0,124	1993	1480	1710
$\alpha$ -Cr	3,91	52,01	7,14	1700	1515	-0,153	-0,136	1880	1410	1590
$\alpha$ -Fe	4,50	55,85	7,87	1980	1770	-0,155	-0,138	1843	1630	1720
Rb	0,855	85,48	1,53	95,4	85,0	-0,039	-0,035	313	87,2	77,5
Cs	0,788	132,91	1,87	77,0	68,5	-0,034	-0,030	301	66,5	55

\*Average experimental values for surface energy taken from [4].

In deducing equation (7), it was assumed that the energy of the relationship between neighboring atoms and the electron concentration within the crystal and on the crystal surface were identical, which does not correspond with what actually exists.

In spite of a few assumptions made in deriving equation (7), it offers us a fair degree of accuracy in calculating the surface energy of metals for various crystallographic planes at any temperature.

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